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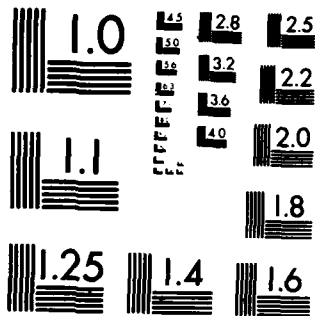
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**CAUSES AND PREVENTION OF STRUCTURAL
MATERIALS FAILURES IN NAVAL ENVIRONMENTS**

V. S. Agarwala, D. A. Berman & G. Kohlhaas
Aircraft and Crew Systems Technology Directorate
NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

1984

PROGRESS REPORT

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
CORROSION FATIGUE AND STRESS CORROSION CRACKING	2
HYDROGEN EMBRITTLEMENT MEASUREMENTS	7
ENVIRONMENTAL MONITORING	9
HEAT TREATMENT	10
ALLOY DEVELOPMENT	11
CONCLUSIONS	12
SUMMARY	13
REFERENCES	14

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CAUSES AND PREVENTION OF STRUCTURAL MATERIALS FAILURES IN NAVAL ENVIRONMENTS

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ABSTRACT

An analysis is made of most corrosion related naval aircraft structural materials failure problems. The phenomena of stress corrosion cracking, hydrogen or environmental cracking, corrosion fatigue and exfoliation corrosion are discussed. Methods of determining hydrogen embrittling effects and hydrogen concentration are described and related to sustained load tolerances of cadmium plated high strength steels. An electro-mechanical test is described to illustrate the hydrogen-induced elastic deformation effect in steels. This test procedure has been also used to calculate the hydrogen diffusion coefficient as well as the hydrogen concentration. A technique which can monitor corrosivity of the naval environment aboard ship has been reported. Metallurgical methods of mitigating corrosion such as heat treatment and alloy development are described. Mechanistic aspects of corrosion-assisted mechanical failures (cracking) are analyzed and a multidisciplinary approach to solve the problem is described. It is demonstrated that modifications of the crack-tip chemistry can effectively lead to inhibition of corrosion fatigue and stress corrosion cracking in high strength alloys.

INTRODUCTION

A wide spectrum of corrosion problems are encountered in naval aircraft due to the unique combination of materials, environment and service conditions. Figure 1 illustrates the action of the environment with time to cause corrosion of materials; the combination of mechanical factors and corrosion to produce structural failures; and methods to control or prevent corrosion and corrosion assisted failures. The simple action of the environment on materials can lead

*Visiting scientist at Naval Air Development Center during 1982-83.

to corrosion (general, pitting, exfoliation) which might manifest itself as a cosmetic problem only, but can also be very serious if deterioration of an aircraft skin or electronic components occurs. Most serious corrosion problems which can lead to catastrophic failure, result from a combination of the environment and mechanical factors, such as stress, fatigue or wear, with the material. Failures from stress corrosion cracking, corrosion fatigue and hydrogen embrittlement fall in this category. The high performance demanded of materials and systems used in today's aircraft offer little room for deterioration in properties. Thus, it is very important to understand the interplay among environmental factors, service conditions and materials.

The materials used in naval aircraft are intrinsically active, and are especially susceptible to the presence of chloride and changes in pH. The high strength requirements limit the full utilization of corrosion resistant properties of lower strength heat treatments. For example, 7075-T6 aluminum is more prone to exfoliation and stress corrosion cracking than 7075-T7, and 4340 steel heat treated to the 260-280 ksi strength level has a shorter fatigue life and is more susceptible to hydrogen embrittlement than if treated to the 200-220 ksi level.

Environmental factors include high humidity, variable temperatures, salt spray, carrier exhaust gases, processing and operational chemicals, etc., all potentially detrimental from a corrosion or hydrogen embrittlement viewpoint.

The conditions under which naval aircraft operate are very severe. Carrier takeoffs and landings, and flight maneuvers subject the aircraft to high dynamic stresses. Even when not in flight, the environmental factors are present, such as liquid intrusion, which can cause contamination of hydraulic and lubricating fluids leading to corrosive wear.

These are only a few of the many types of corrosion problems which can be encountered. When catastrophic failures occur, the cost in lives, equipment and time is great. Conservative estimates place the monetary cost of corrosion to the air navy at greater than half a billion dollars per year. By knowing how, why and where corrosion occurs, solutions and/or maintenance procedures can be provided which, in the long run, can save large sums of money.

Much can be done to reduce corrosion problems by design changes, the proper use of alloys, the elimination of moisture traps, etc. These aspects are beyond the scope of this paper. We shall concern ourselves with recent progress made in corrosion prevention and control, specifically in the area of "wet corrosion," and not with high temperature oxidation. Examples will be given of techniques used to investigate corrosion processes, procedures and products developed to minimize corrosion, environmental monitoring and modification of processing conditions and procedures.

CORROSION FATIGUE AND STRESS CORROSION CRACKING

Corrosion damages of general (cosmetic) nature are easily combated by conventional methods such as surface modifications (organic and inorganic films, thermal treatments, etc.), cathodic or anodic protection (galvanic coupling, passivation, etc.) and environmental modifications. But inhibit-

ion of corrosion-assisted mechanical damage requires a multidisciplinary (electrochemical, metallurgical and mechanical) approach because the phenomena of stress corrosion cracking (SCC) and corrosion fatigue (CF) are not defined in terms of their mechanisms of failure in any one particular discipline. In high strength aerospace alloys it is even more complex as the interactions of environment and stress are more subtle. It has been accepted that hydrogen plays an important role in the cracking process. Considerable work has been done in this area and some methods to determine its role are described here under "hydrogen embrittlement".

The mechanisms of corrosion fatigue and stress corrosion cracking are analogous in many respects, and often are described as an extension of one another in terms of frequency and magnitude. Since corrosion is a time dependent phenomenon, the major differences in their mechanisms are generally in the magnitude of their anodic and cathodic processes. The failure mechanisms involved are almost the same - they are time dependent, macroscopic and related to electrochemical, metallurgical and mechanical aspects of surface interactions in fine crevices such as cracks. These have been isolated as follows:

- (i) the anodic processes in which the dissolution of metals occurs - the apex of the stress vector acts as the anode;
- (ii) the cathodic process in which reduction of the proton leads to generation of atomic hydrogen as the first step;
- (iii) creation of elastic-plastic zones near the crack tip region due to movement of dislocations under applied stresses (cyclic or static);
- (iv) the emergence of slip steps resulting in the generation of new surfaces which are highly reactive; and
- (v) an increase in surface energy (surface tension) causing accelerated adsorption of environment.

The most distinguishing features between a corrosion fatigue failure and one caused by stress corrosion is that CF almost always manifests itself in transgranular cracking whereas SCC may be either transgranular or intergranular depending on the magnitude of anodic dissolution. With CF, corrosive action (anodic process) merely serves to trigger the brittle fracture, whereas in SCC, the corrosive action not only serves to initiate the cracking, but is required to propagate it further. Often hydrogen cracking (embrittlement) and SCC are used interchangeably in describing a failure because hydrogen plays an important role in the cracking process.

Electrochemically, the phenomena of SCC and CF can be simplified in terms of their anodic and cathodic polarization responses as shown in Figure 2. In Figure 2a, the polarization behavior of an active-passive alloy under static test is shown. This is typical of SCC behavior where corrosion potentials shift from a passive to active region when cracking occurs, even though the alloy may normally be passive in a given environment. At times when a crack does not propagate, passivity may occur again. In the cyclic test, the polarization behavior does not change, and the corrosion potential remains active, as shown in Figure 2b. The anodic polarization curve shows

hardly any passive behavior. This is very typical of CF behavior in a moist environment. The presence of a spontaneously passivating chemical compound in the crack can reduce the SCC and CF behavior of the alloy. This is shown in Figure 2c. But when an environment contains chloride, a breakdown in passivity (shown as the bold curve in Figure 2d) occurs, and the breakdown potential for pitting shifts to a more active potential resulting in higher current densities. Passivating inhibitors like chromates are inadequate to reduce cracking in the presence of chloride ions due to this effect. Thus chloride counteracting agents are required which can reinforce passivity or shift the breakdown potential for pitting to more noble values and very low current densities. The dotted line in Figure 2d represents this desired condition.

Principally, the modification of crack tip chemistry (electrochemistry) can provide solutions to the problem as illustrated, but one must bear in mind that these modifications must take place in fine crevices.

Crack Arrestment Compound

The development of a chemical system which can be applied in-situ to arrest cracking in high strength alloys is an ongoing independent research program at the Naval Air Development Center (1). Based on the mechanisms of failure described earlier, a number of chemical compounds were selected and studied. The basic requirements of selection were that each compound must have at least one of the following capabilities: promote formation of a passive film (barrier effect), minimize hydrogen entry or absorption, modify crack-tip pH and displace moisture. Most of the chemicals were inorganic reduction-oxidation (redox) systems which were phase transferred into an organic solvent through a quaternary ammonium salt for formulation. In this manner, the redox properties of various compounds were retained in the mixture and the medium provided the water displacing high transport property to the system. The transport of inhibiting species to the crack tip is very essential for the arrestment of cracking. The details of the method of formulation and selection criteria have been described elsewhere (2). One combination of chemicals will be discussed here. This is a mixture of sodium salts of dichromate, nitrite, borate and molybdate (DNBM) dissolved in mineral spirits using methyl trialkyl(C_8-C_{10}) ammonium chloride (Aldrich Adogen 464) as a phase transfer catalyst. This combination (DNBM) was evaluated for its effect on the corrosion fatigue and stress corrosion cracking behavior of 4340 steel (1800-1900 MPa) and 7075-T6 aluminum alloy (500 MPa). The environment selected was moist air laden with salt (sodium chloride). In all cases, fracture mechanics type specimens were used, and the crack arrestment compound (DNBM) was applied at the notches only after precracking. Fracture mechanics type specimens were chosen because crack growth measurements give more information than time-to-failure determinations using tensile or C-ring specimens (ASTM Method F-519). Also, the precision is better because the pre-cracked specimen grows only a single crack and does not have an induction time.

In the corrosion fatigue studies, ASTM method E-399 was used and the crack growth rate measured in crack extension per cycle (da/dN). The results, plotted as da/dN versus stress intensity factor (ΔK) for 4340 steel are shown in Figure 3. A comparative evaluation of the nature of the

curves show that the DNEM has the lowest crack growth rate at all stress intensities, and counteracted the effect of a chloride environment by a factor of approximately six in terms of fatigue life.

In the stress corrosion cracking studies, the method of Hyatt (3) was adopted, and double cantilever beam specimens were used. The crack growth rate (da/dt) measured in mm/hr was determined and plotted against the stress intensity factor (K_I). The curves for 7075-T6 alloy are shown in Figure 4. Here, the threshold values for K_I (K_{ISCC}) determined from the above plot indicate the SCC susceptibility of the material. K_{ISCC} is the value (the vertically straight portion of the plot) where the stress intensity becomes almost independent of crack growth rate. The higher the K_{ISCC} , the higher the resistance to SCC. In 100% humidity with chloride the K_{ISCC} value was significantly higher with the DNEM combination than with no inhibitor (cf. curve 3-3 with curve 2-2 in Figure 4). At a stress intensity factor of approximately 550 $KPa\sqrt{mm}$ DNEM retarded the crack growth rate by a factor of 8.

Microfractography

Microscopic examinations of the fracture surface are very helpful in determining the failure mode. Scanning electron microscopy (SEM) provides the best method for identifying the brittle and ductile fractures with excellent resolution. The SEM micrographs of 4340 steel specimens after fatigue tests are shown at the left in Figure 5. The morphology of the test done in dry air (less than 15% RH) shows fatigue striations and shear lips (honeycomb) typical of ductile failure. The micrographs in the lower left corner representing the CF failure in salt-laden moist air is entirely different, and has a rock candy appearance with intergranular cracks. This is typical of brittle fracture or hydrogen embrittlement failure. The micrograph "with inhibitor" on the immediate right shows a morphology which is in-between the last two fracture profiles, i.e. partly brittle (rock candy) and partly ductile (honeycomb), indicating the effect of DNEM on the degree of embrittlement.

The beneficial effect of DNEM on the SCC behavior of 7075-T6 alloy is better shown in the total length of the crack growth during the first 2000 hours of exposure. This is shown in Figure 5 on the right. A comparison of the crack lengths between the specimens without and with inhibitor (in the rectangular shapes) shows the crack growth retardation effect by the inhibitor. The SEM micrographs of the SCC region (distinguished by a high crack growth rate and shown as circles) show the fracture mode. The one on the extreme right shows ductile (honeycomb) features due to the presence of DNEM whereas the circle on the left shows brittle fracture (when observed up to 5000 magnification) with a high degree of intergranular cracking. The bottom half of the circle shows the overload fracture after the specimen was cracked open - a distinctly distinguishing feature compared to the top half. A better and more detailed discussion of the microscopic mechanisms, as revealed by fracture surface markings, is given in the handbook on Fracture (4).

Electrochemical Polarization Studies

The performance of the individual compounds used in the formulation (DNEM) for the arrestment of cracking were investigated electrochemically

for various functional properties. The dichromate, nitrite and molybdate were studied for their passivating, oxygen-scavenging and chloride resistance properties. Electrochemical hydrogen permeation experiments were performed for hydrogen inhibition effect by dichromate and molybdate. It was found that during cathodic reactions, the entry of the hydrogen evolved into the metal can be delayed by these compounds by several factors. Potentiostatic anodic and cathodic polarization measurements were performed to determine the corrosion inhibition effect by these compounds according to the ASTM method G3-74. The details of this and other electrochemical techniques used in various corrosion studies have been better reported elsewhere (5). As an illustration, the effects of nitrite and molybdate compounds on the polarization behavior of 1020 steel in 1% NaCl (pH2) are shown in Figure 6. It was found that none of the inhibitors could show spontaneously passive behavior in the presence of chloride. The anodic polarization curves in each case were different but the cathodic curves were almost the same, thus only one was drawn in Figure 6. Among the inhibitors only the molybdate compound demonstrated some active to passive transition whereas the others continued to remain active even at higher potentials (in the noble direction). However, the combination of nitrite and molybdate showed a significant passive range (— curve). At a higher concentration (0.05M compared to 0.01M) of the inhibitors, the 1020 steel was spontaneously passive (-x-x- curve) as the corrosion potential shifted to very noble values. Thus a mixture of nitrite and molybdate was complementary in properties in aqueous medium. The additions of dichromate and borate to this mixture were not synergistic in action. In an organic medium, the identity of each compound was retained, as in the DNBM formulation in mineral spirits, and made available when cracking inhibition was needed. Mechanistically in the mixture of DNBM, dichromate served as a good passivator, molybdate as a pitting inhibitor (resistance to chloride attack), nitrite as an oxygen scavenger and as a passivity restorer, and borate as a pH modifier. Additionally, dichromate and molybdate-inhibited hydrogen absorption by the metal.

HYDROGEN EMBRITTLEMENT MEASUREMENTS

Hydrogen can enter a metal during plating or corrosion, migrate to regions of high stress, and weaken the cohesive forces of the material. High strength steels are especially susceptible to hydrogen embrittlement, and can undergo catastrophic failure. Because hydrogen might also be retained in irreversible traps or as stable hydrides, the measurement of total hydrogen is not always meaningful with regard to hydrogen embrittlement. Electrochemical methods are especially applicable to the study of the uptake, mobility and retention of mobile hydrogen, and thus can be used to investigate materials and processes for possible hydrogen damage problems.

Electrochemical Hydrogen Permeation

In the electrochemical permeation method, hydrogen is made to enter from one side of a thin metallic sheet and exit through the other side. The entry side of the specimen is the cathode in an electrochemical charging or plating circuit; the exit side is the anode in a potentiostatic circuit. The hydrogen which diffuses to the surface at the exit side is oxidized. The oxidation current versus time curve can then be analyzed to give information concerning permeation of hydrogen through the metal. Details of the technique can be found in the literature (6).

This method has been used to study the effect of inhibitors on the hydrogen diffusion through metals as shown in Figure 7. As cathodic charging proceeds, hydrogen is produced, permeates through the specimen, and builds up to a maximum concentration as shown by the steady state oxidation current. At this point, sodium tellurate is added to the charging solution. There is a dramatic drop in hydrogen permeation current due to the reduction of the tellurate, rather than of the hydrogen ion. Subsequently, the permeation current slowly increases, but does not reach the original value due to the slight barrier effect of tellurium which has been deposited. Thus it has been shown that the tellurate ion, an electron acceptor, can delay the production of hydrogen. If sodium tellurate is added to a plating bath, this may delay the production of hydrogen, thus reducing the total hydrogen pickup during conventional plating. Used as an inhibitor, it could also reduce the hydrogen uptake during the corrosion process.

Barnacle Electrode

The barnacle electrode system, developed in this laboratory, is an adaptation of the permeation method to determine mobile hydrogen which is already in the metal (7). In this technique, the charging circuit is no longer needed, and the extraction circuit has been simplified by replacing the potentiostat, and reference and counter electrodes with the fairly stable non-polarizable nickel/nickel oxide electrode. Again, the hydrogen oxidation current can be related to the hydrogen concentration.

The barnacle electrode has been used to determine the efficiency of the post-plating backout procedure as a method of reducing hydrogen embrittlement (Table 1). A main cause of hydrogen embrittlement in high strength steels is the hydrogen introduced during plating. Standard procedure calls for relieving hydrogen embrittlement by baking at 190°C for up to 24 hours. As can be seen from Table 1, this time is inadequate. Even after 96 hours, some hydrogen

remains. If a wide range of stresses is used along with different hydrogen concentrations, a complete indexing of the degree of embrittlement of a susceptible alloy can be obtained. Figure 8 shows the threshold curve indicating safe and unsafe hydrogen concentrations for a cathodically charged unplated 4340 steel. Comparing this with the results shown with a cadmium plated steel in Table 1, it can be seen that an indexing curve for plated material would shift to a more dangerous position.

Hydrogen Induced Deformation

A somewhat different approach to the hydrogen embrittlement problem is from the viewpoint of its effect on the metal lattice (8, 9). Interstitially dissolved hydrogen in the metal lattice causes local disorders of an elastic nature. Accumulation of lattice disorders in one region of the specimen volume creates stresses which may result in a macroscopic deformation of the specimen and permanent damage to the material in high stress areas. The accumulation of local disorders can be created by electrochemical charging. If, for example, a specimen in the shape of a bar, Figure 9a, is cathodically charged on one side, it will bend, as shown schematically in Figure 9b. The degree of this bending depends upon the hydrogen concentration gradient through the thickness of the specimen. Since the hydrogen concentration profile shown in Figure 9b changes with time, so does the bending. This bending goes through a maximum, Figure 9c, which is characteristic of the material, and which can be used for calculating the diffusion coefficient and the hydrogen concentration.

The hydrogen induced deformation experiment, developed in this laboratory, was performed using two flat bars joined together as shown in Figure 10. The open ends of the bars were connected to a strain gage extensometer through lever arms which provided the necessary amplification for measurement. All exposed parts except for the charging areas were masked with beeswax. Transient measurements of deflections were made using an amplifier and strip chart recorder. Cathodic charging of the internal faces of the specimens was initiated after a steady state background deflection was obtained. Charging was continued until the deflection passed through a maximum. This deflection can be used to calculate the diffusivity, D , which is proportional to the time of maximum deflection, t_{\max} , according to

$$D = \frac{0.08513 L^2}{t_{\max}} \quad (1)$$

where L = specimen thickness. The hydrogen concentration is a function of the deflection, and can be calculated by

$$\frac{C_1}{C_0} = \frac{1 + E_c \times Y_{\max}}{48 \times 0.12568 K_{\text{geom}}} \quad (2)$$

where C_1 = maximum hydrogen concentration

C_0 = initial hydrogen concentration

Y_{\max} = maximum deflection

$$K_{\text{geom}} = \frac{A}{L} \left(S + \frac{A}{2} \right)$$

where A = specimen length and S = lever length; and E_c = concentration strain modulus.

The numerical values in equations (1) and (2) were determined from theoretical solutions of the test model, the details of which are beyond the scope of this paper. E_c is a newly defined material constant which must be determined independently. From a deformation experiment on annealed 4340 steel, D was found to be $1.28 \times 10^{-5} \text{ cm}^2/\text{s}$, and C_1/C_0 to be 4.1. To determine C_1 , C_0 must be determined independently. The value of E_c determined for 4340 steel was 1.5×10^6 . The diffusivity calculated here is higher than that determined by conventional electrochemical permeation methods (6), due to the fact that the D calculated from Eq (1) is determined from maximum mechanical effects (bending) whereas the other method does not. This is consistent with the results of previous experiments in which stressing has been shown to increase hydrogen diffusion (8, 9). This explains why hydrogen embrittlement can occur even in materials of low hydrogen diffusivity.

ENVIRONMENTAL MONITORING

Currently, the assessment of corrosivity of an environment is based on projections from on-site long term exposure tests. Tests such as salt fog, total immersion and alternate immersion were primarily designed from such projections to produce accelerated laboratory test environments. In situations such as in the navy where rapid changes in the weather occur, a true evaluation of the corrosivity of the environment is not possible. Any extrapolation of the results from laboratory tests may be inaccurate at best, and deceptive at worst. Therefore, it is important that an assessment of the actual corrosivity of the environment be made before a simulated laboratory test environment can be developed. In particular, a quantitative determination of the corrosivity of the aircraft carrier environment is of great interest, since the carrier environment is known to be most severe and changes rapidly from mission to mission.

Electrochemical Corrosion Monitor

Based on the principles of an electrochemical galvanic cell, a device has been developed to measure corrosivity of the environment. It consists of a probe or sensor and a high impedance current monitoring system. The sensor is a galvanic couple made of several plates of two dissimilar metals such as copper and steel (iron). The current monitoring system is a zero resistance ammeter interfaced with a digital data logger. The details of the principles involved, and the technique are described elsewhere (10). For the present, it will suffice to mention that the magnitude of the cell current developed by the sensor in an environment (moist environment containing pollutants) is a direct measure of its corrosivity. Evaluation of this device has been made by exposing the sensor to both the laboratory test environment and aboard ships including an aircraft carrier. The results of one such test are given in Figure 11 which shows the corrosivity of the environment during a mission of the research ship USNS Vanguard. The severity of the environment can be easily compared with an accelerated laboratory test, shown in the inset in Figure 11, for a more quantitative relationship. The tests (monitoring) carried out in the aircraft carrier flight deck environment have shown a very high corrosion activity which was similar in magnitude to that recorded in the 5% NaCl spray chamber with SO_2 cycling (11).

HEAT TREATMENT

Heat treatment is generally the preferred way to improve mechanical properties, such as high modulus, high strength, etc., of alloys (steels and aluminum). These properties make materials ideally suited for use in high performance aircraft; but the susceptibilities of such materials to stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, exfoliation or intergranular corrosion in marine (aircraft carrier) environment make them less desirable. In the case of 7000 series aluminum alloys, it was discovered that if these alloys were systematically overaged, their susceptibilities to SCC and exfoliation corrosion would be drastically reduced. For instance, in 7075 alloy, T73 overaging treatment has replaced the temper T6 on many military aircraft. However, a penalty of approximately 20% strength loss was realized and some designs had to be altered to compensate for this loss.

Retrogression and Re-Aging

Recently, it has been demonstrated (12) that a pre-aging treatment for 7075 aluminum alloy improves its resistance to SCC without sacrificing the maximum strength of the T6 temper. This process which is called retrogression and re-aging (RRA) is a two-step treatment after the alloy has been heat treated to the T6 condition. First, the material (7075-T6) is "retrogressed" at a temperature between 200-260°C for a short time, water quenched, then re-aged at the original aging temperature of 120°C. The details of this procedure are described elsewhere (12, 13). To illustrate the corrosion behavior of such RRA-treated one-inch thick 7075-T6 plate, both SCC (ASTM Standard G38) and exfoliation corrosion (ASTM Standard G34) susceptibility tests were carried out. The study of the crack growth rate (da/dt) with decreasing stress intensities (K_I) in a 3.5% NaCl solution at pH2 was also performed. It was found that RRA-treated material had almost the same behavior as T73 tempered material. Figure 12 shows the results of a da/dt vs K_I plot for SCC behavior of both the T6 and RRA treated specimens. The SCC threshold, $K_{I_{SCC}}$, for RRA-treated material was much higher than for T6 alone. The photographs adjacent to each curve (treatment) in Figure 12 show the exfoliation corrosion behavior. The RRA specimen shows only slight corrosion, an improvement from EB to EA according to ASTM Standard G34, indicating a significant resistance to intergranular corrosion. The hardness of the 7075-T6 alloy was only slightly sacrificed, i.e. from 94-95 to 88-89 R_B , after the RRA treatment. The future in this area is quite promising.

ALLOY DEVELOPMENT

Classically, modifications of alloy composition to enhance corrosion-resistant behavior of many ferrous and non-ferrous alloys have been made in the past. For instance, additions of Cr, Ni and/or Mo in steels gave way to so-called stainless steels. Additions of Cu to aluminum alloys (2000 series), Zr to Al-Zn-Mg alloys, etc., have lessened corrosion susceptibilities. In particular, alloy 7075 which was developed under Naval Air Systems Command guidance (14) has shown excellent stress corrosion cracking resistance with the highest strength of any commercial aerospace alloy.

Powder Metallurgy

Recently the advent of powder metallurgy provided a new dimension in alloy development programs (15). It has provided a new approach to develop high modulus, high strength alloys without much sacrifice of corrosion resistance. In general, the powder metallurgy (PM) alloys have better corrosion behavior than their ingot counterparts. This is primarily due to better control of impurities and a reduction of grain orientation or directionality in PM materials. Highly amorphous microstructures are generally more corrosion resistant. Additionally, under a PM process, the level of a particular substance (e.g. elements which improve corrosion resistance) can be increased beyond the solid solution solubility limits which is not possible in ingot metallurgy. Powder size and compaction techniques can further beneficially change the overall corrosion behavior of the alloy.

Advances have also been made using the powder metallurgy approach in the development of composites where high stiffness and directionality are required. Metal-matrix composites which contain fibers of aluminum oxide, silicon carbide, boron, etc., in aluminum alloy matrix are currently being studied for their metallurgical, mechanical and corrosion properties. These alloys have generally higher corrosion resistance but could suffer from microstructural corrosion and thus may lose their load transfer capabilities from matrix to fiber, the most desired property of composites. This effort is worth watching for aerospace applications.

CONCLUSIONS

A variety of results from a multidisciplinary effort in the study of corrosion problems was reported. These are:

- 1) A crack arrestment formulation (DNBM) containing a mixture of inorganic compounds (sodium salts of dichromate, nitrite, borate and molybdate) in an organic vehicle was shown to be effective in reducing crack growth in both CF and SCC experiments. Fatigue life of 4340 steel was increased six times in a chloride containing environment. The SCC crack growth rate was decreased by a factor of 8, and the K_{ISCC} was significantly improved.
- 2) Microscopic examination of fracture surfaces from the above tests showed less brittle failure in the presence of DNBM.
- 3) Electrochemical studies on the components of DNBM showed that dichromate is a good passivator, molybdate inhibits pitting in chloride, nitrite is an oxygen scavenger, and borate is a buffer.
- 4) Electrochemical hydrogen permeation experiments showed that sodium tellurate, sodium dichromate and sodium molybdate delay the entry of hydrogen into a metal during cathodic charging.
- 5) Barnacle electrode measurements showed that even after baking for 96 hours, a cadmium-plated steel (300M) contains some mobile hydrogen and will fail if loaded to 75% NTS.
- 6) A hydrogen embrittlement threshold curve for unplated 4340 steel was given.
- 7) A hydrogen induced deformation experiment was described, and equations for calculating the hydrogen diffusion constant and hydrogen concentration were developed. The value for the diffusivity of hydrogen through annealed 4340 steel was determined to be $1.3 \times 10^{-5} \text{ cm}^2/\text{s}$.
- 8) An electrochemical environmental monitor was described. It was shown that a naval environment could be related to simulated laboratory tests, such as salt/SO₂ spray.
- 9) A retrogression and re-aging heat treatment was described. The exfoliation and SCC behavior of 7075-T6 after RRA treatment is similar to that of 7075-T73.

SUMMARY

This paper reports the efforts of a multidisciplinary approach used to investigate corrosion-related materials failure problems in naval aircraft. Described are mechanisms of failure, techniques to study corrosion behavior, and methods to alter the materials and processes for corrosion prevention. The types of corrosion discussed are those associated mainly with the interaction of the harsh naval environment and rigorous mechanical demands of high strength aircraft materials: stress corrosion cracking, corrosion fatigue and hydrogen embrittlement.

Due to the electrochemical nature of corrosion, and the stress and fatigue related problems, the laboratory approach shows a heavy emphasis on electrochemical and mechanical methods. Crack arrestment compounds for steels and aluminum alloys were evaluated in crack growth experiments using fracture mechanics type specimens in both stress corrosion and corrosion fatigue methods; the mechanisms of inhibition were studied using electrochemical polarization experiments; and the failure types were determined by microfractography. Hydrogen embrittlement of high strength steels was also studied by both electrochemical and mechanical means. The effect of an inhibitor on hydrogen absorption was determined by the electrochemical permeation method; the effectiveness of baking a plated steel was determined by measuring hydrogen using the barnacle electrode as well as by sustained load testing; and an electro-mechanical test was described which can be used to determine hydrogen concentrations and diffusivities by measuring the hydrogen induced elastic deformation. An electrochemical corrosion monitor capable of measuring corrosivity aboard ship was described and results were related to laboratory corrosion tests.

Some ways to mitigate corrosion related problems have been mentioned - inhibitors and baking. Also discussed are modifications of the material by new heat treatments such as retrogression and re-aging or by novel processing such as powder metallurgy to improve corrosion resistance.

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Table 1. Effect of Baking on Hydrogen Content and Embrittlement of Cadmium Plated 300M Steel Stressed to .75% NTS.^{a,b}

Baking Time ^c	Barnacle Electrode Measurement ^d , Oxidation Current	Time-To-Failure
24 hr	0.60 $\mu\text{A}/\text{cm}^2$	0.5 hr
48	.58	5
72	.42	19
96	.38	31

^aNotched Tensile Strength, 1790 MPa (260 ksi)

^bBright cadmium plate, 0.015 mm (0.0005 in)

^cBaked at 190°C (375°F)

^dBackground measurement is 0.35 $\mu\text{A}/\text{cm}^2$

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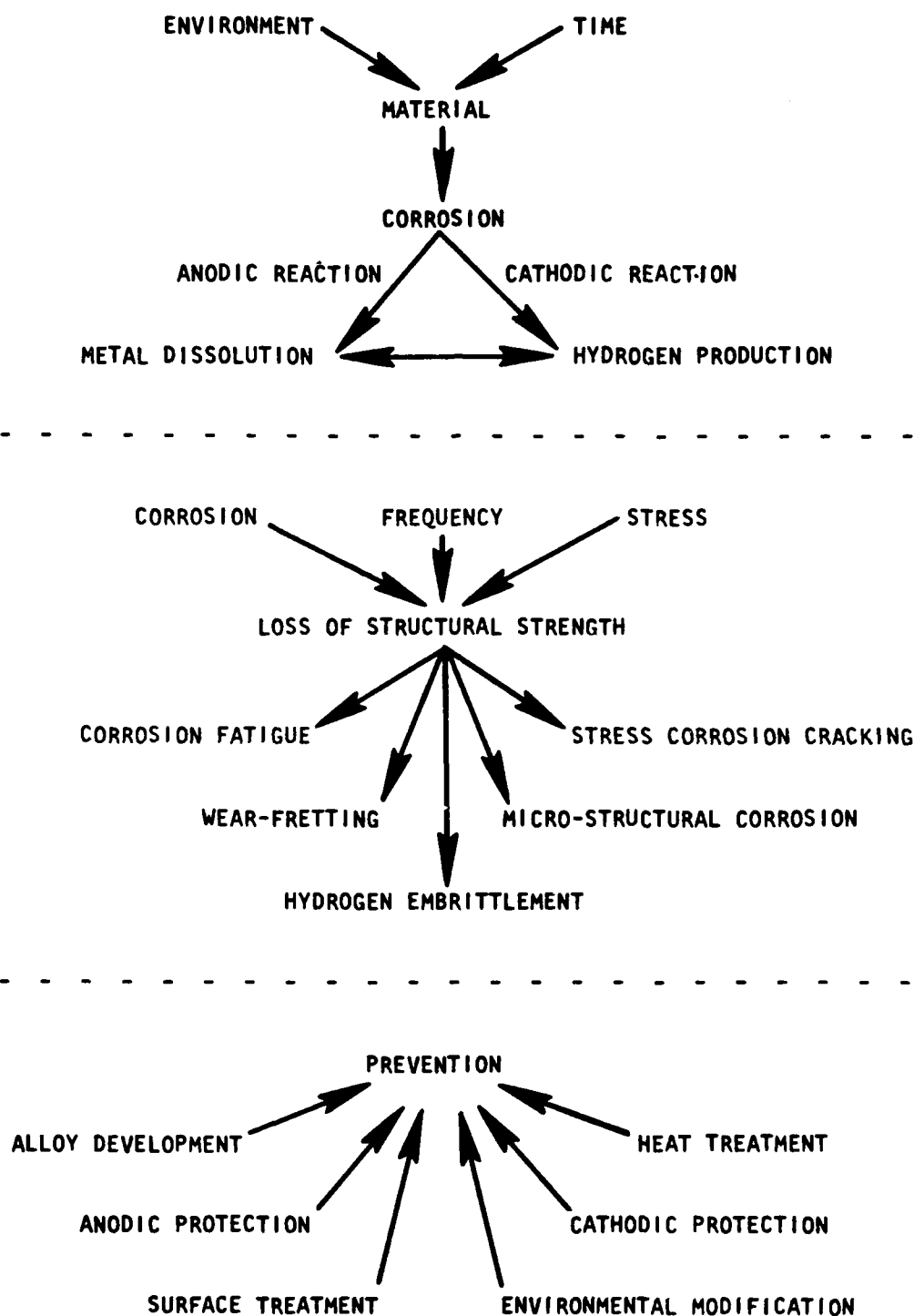


Figure 1. Elements of corrosion, corrosion-induced failures and control in structural materials.

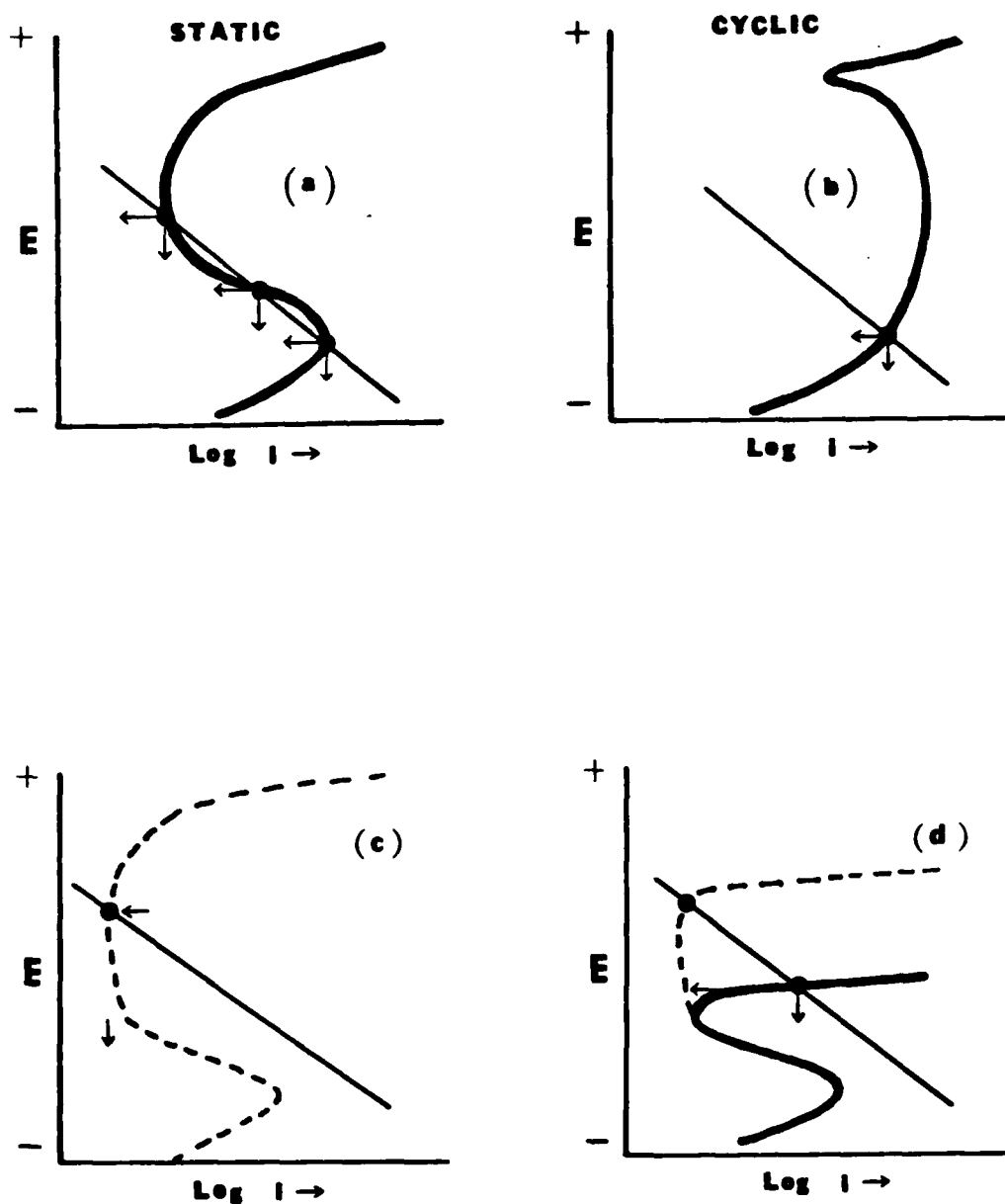


Figure 2. Schematic potentiostatic polarization behavior of an active-passive alloy undergoing stress corrosion cracking (a) and corrosion fatigue (b) in moist air; the same in the presence of a passivating inhibitor (c) and when chloride counteracting inhibitors are present (d). Solid anodic curve shows the effect of chloride; dotted curves (c) and (d) are the results due to inhibitors

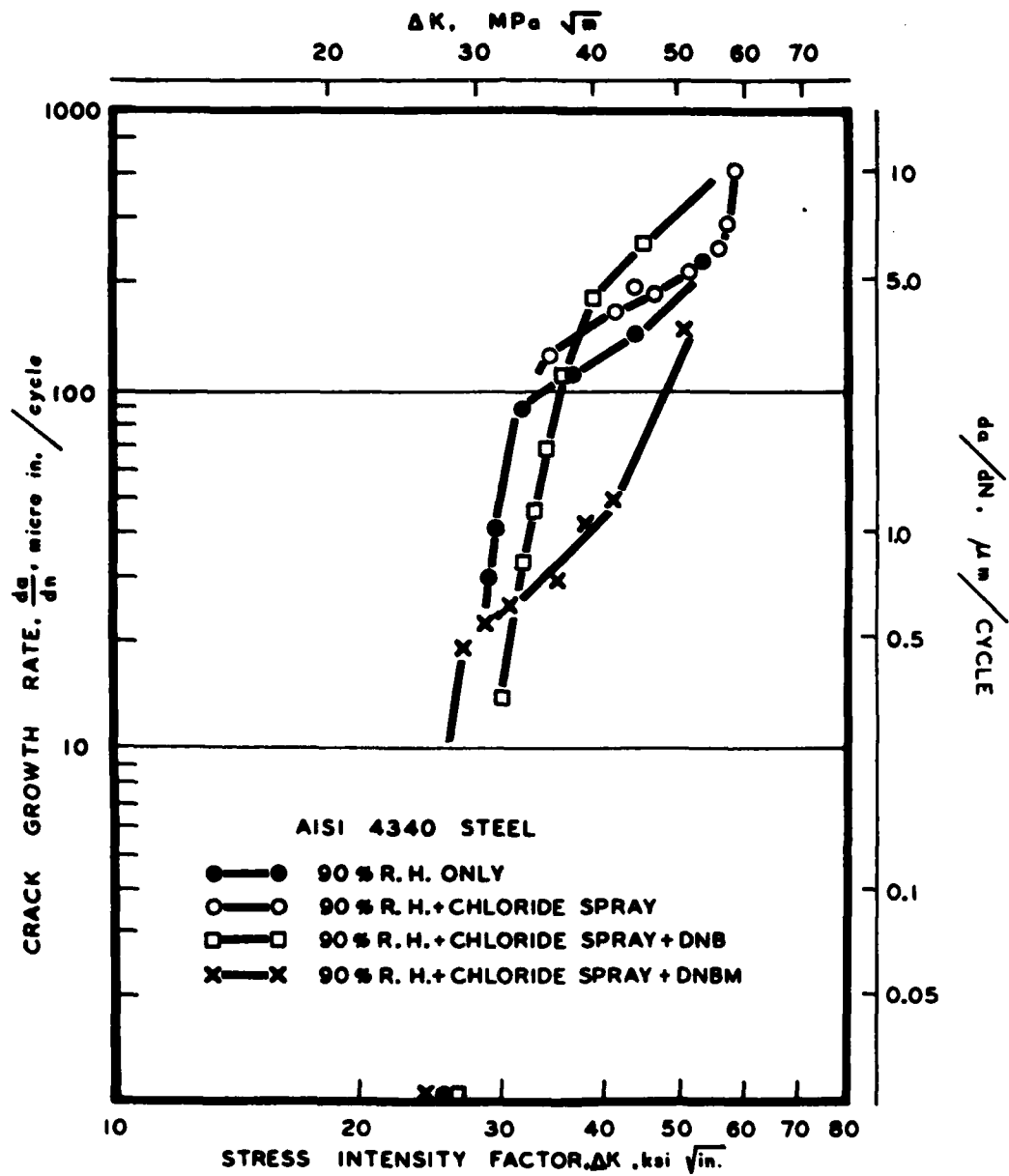


Figure 3. Crack growth rate - stress intensity relationship for 4340 steel during corrosion fatigue.

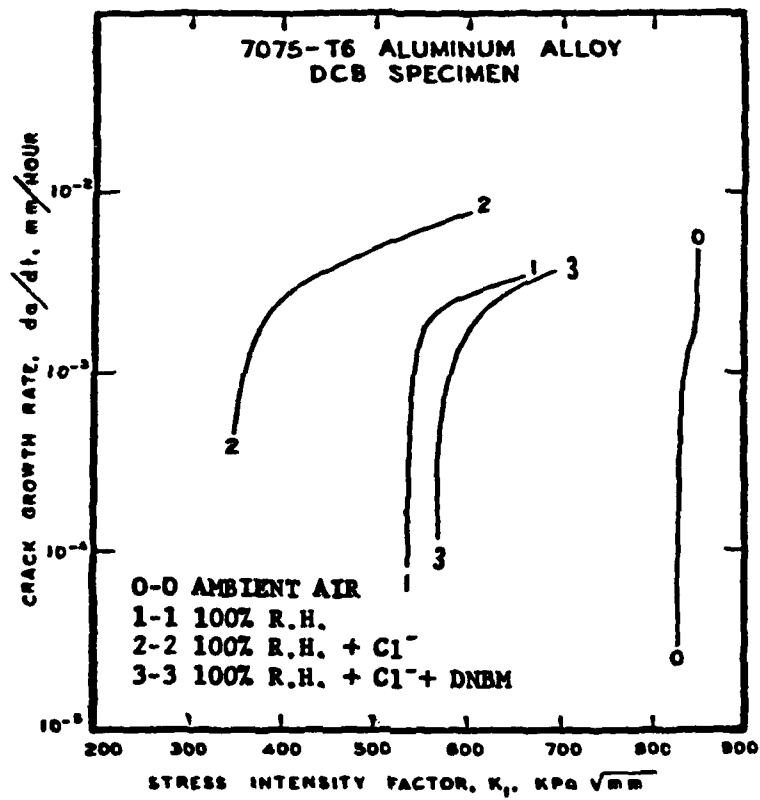


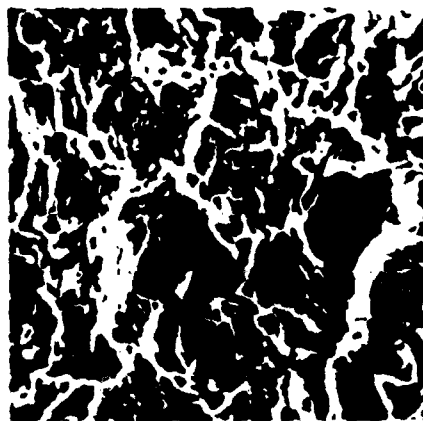
Figure 4. Crack growth rate - stress intensity relationship for 7075-T6 alloy during stress corrosion cracking.

HIGH STRENGTH 4340 STEEL

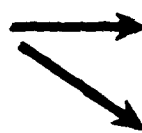
AI 7075-T6 ALLOY

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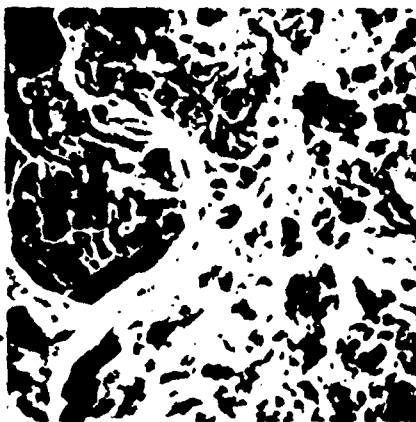
IN DRY AIR



IN MOIST AIR
WITH CHLORIDE



WITH INHIBITORS



CORROSION FATIGUE



WITHOUT
INHIBITORS

WITH INHIBITORS



IN MOIST AIR WITH CHLORIDE



STRESS CORROSION CRACKING

Figure 5. Fractographs of corrosion fatigue and stress corrosion cracking failures.

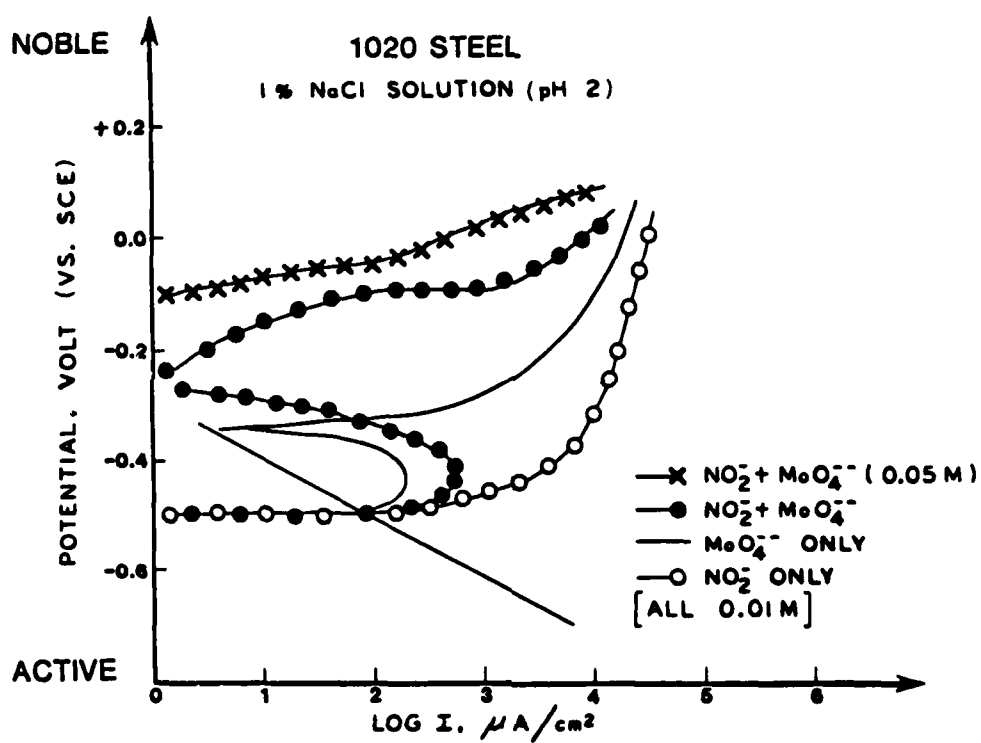


Figure 6. Polarization behavior of 1020 steel in the presence of corrosion inhibitors.

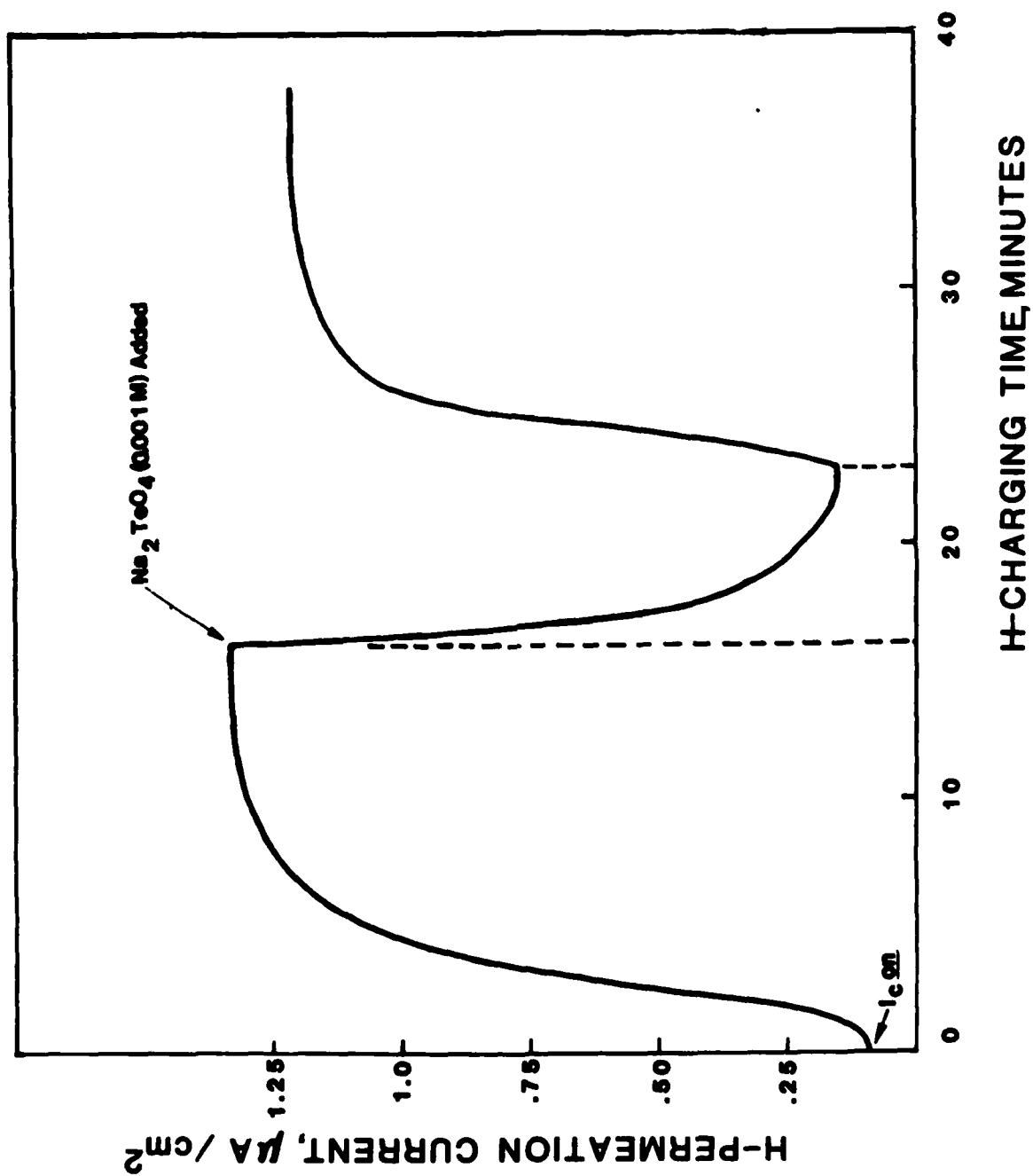


Figure 7. Effect of sodium tellurate on hydrogen permeation transient of Armco iron in 0.2M NaOH + 0.2M NaCN.

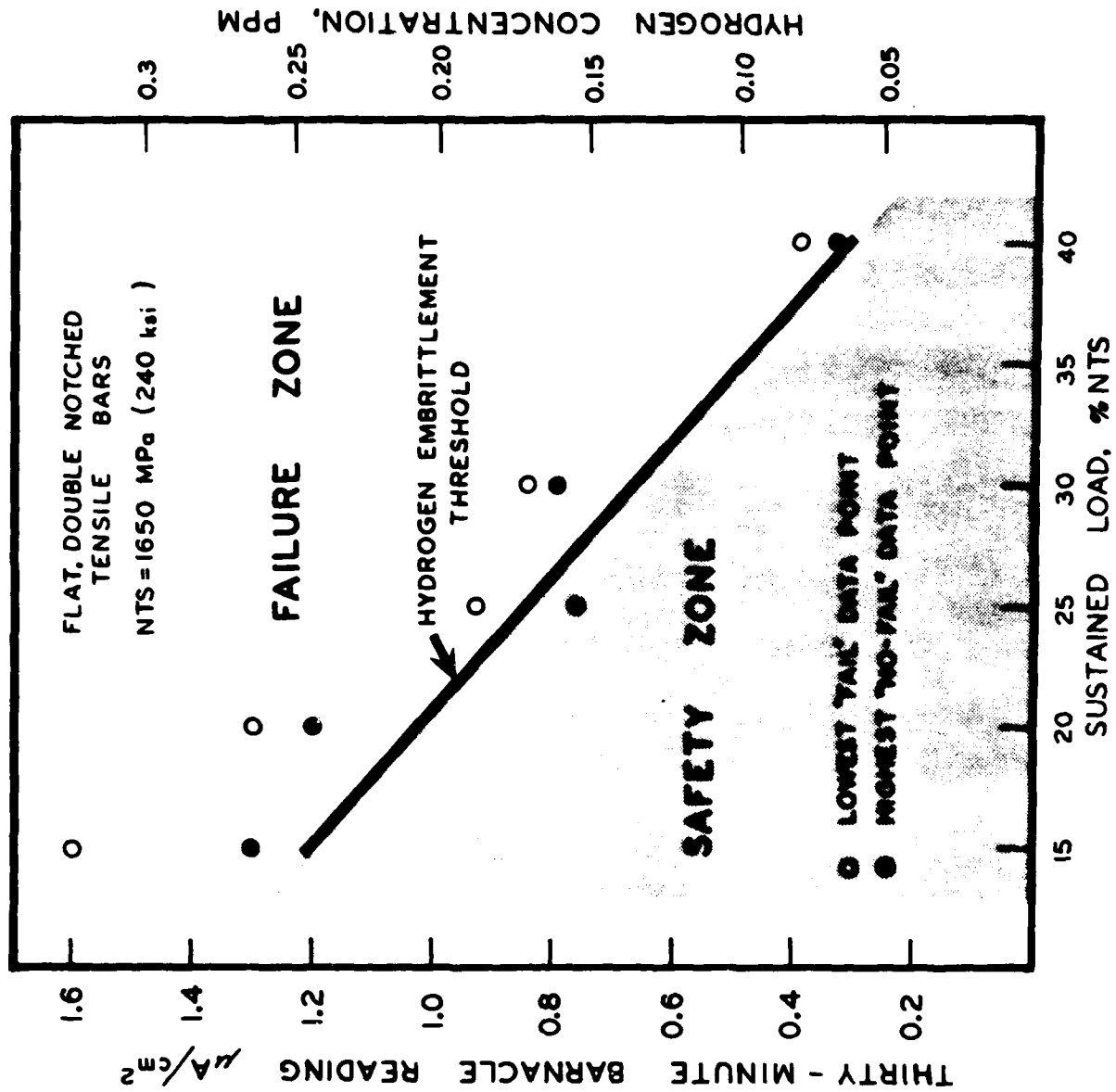


Figure 8. Hydrogen embrittlement threshold plot for 4340 steel.

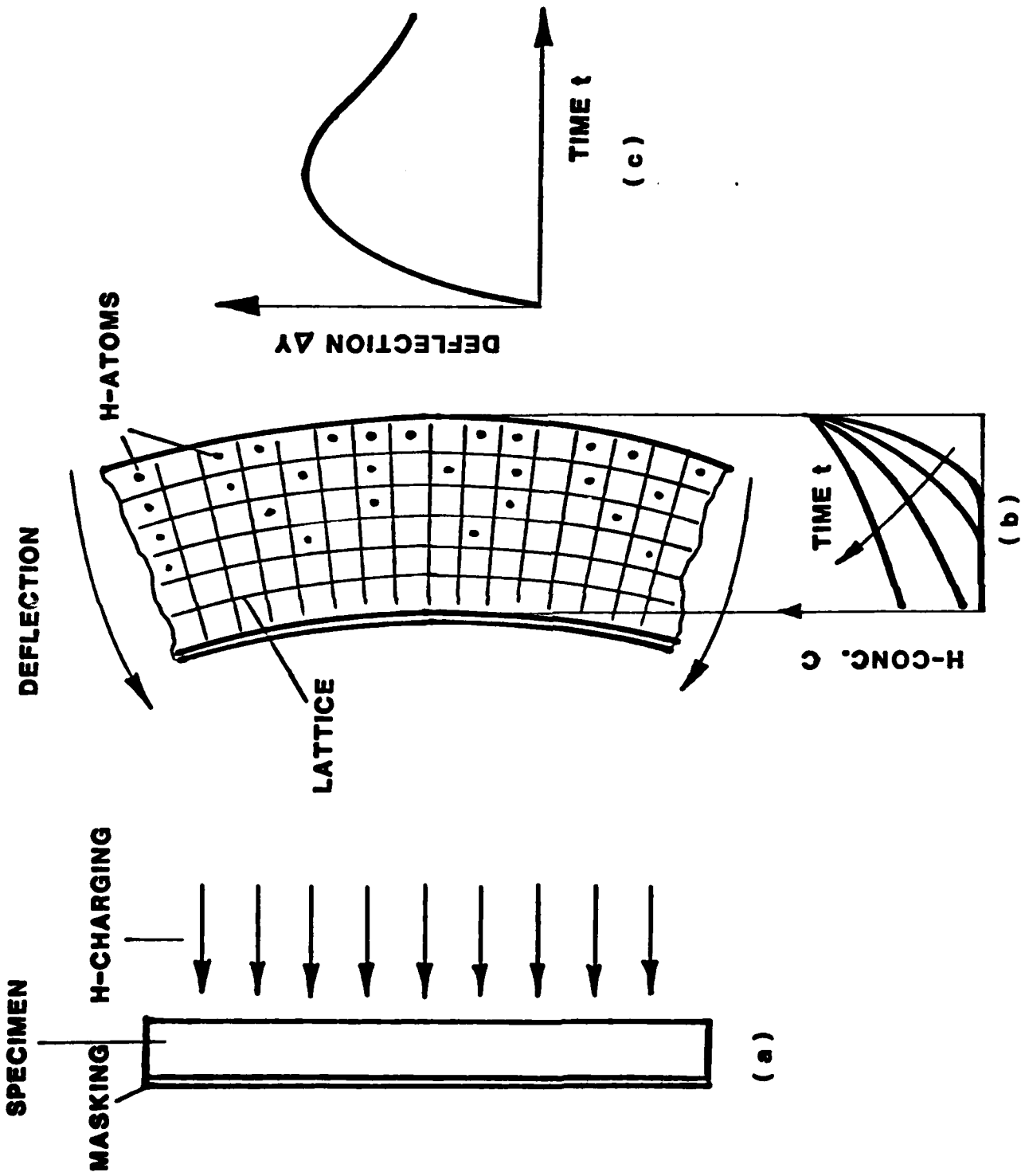


Figure 9. Schematic diagrams of hydrogen induced deformation (bending) showing a specimen (a), bending due to lattice expansion (b) and bending vs time relationship (c).

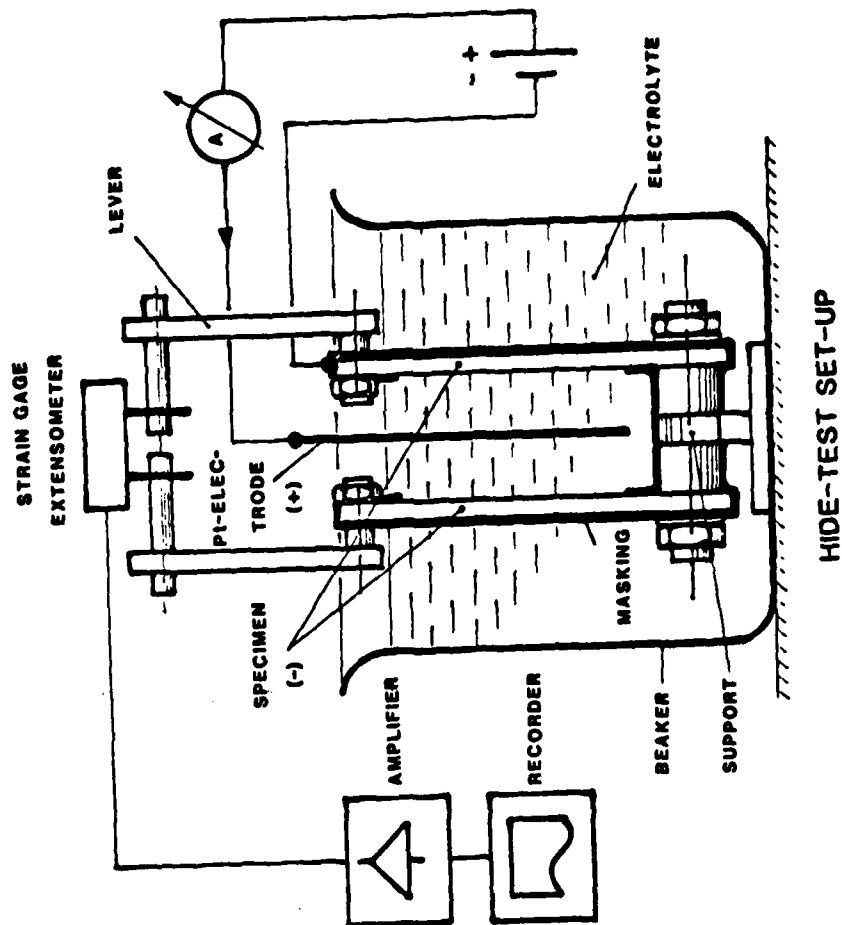


Figure 10. Schematic of hydrogen induced deformation experiment.

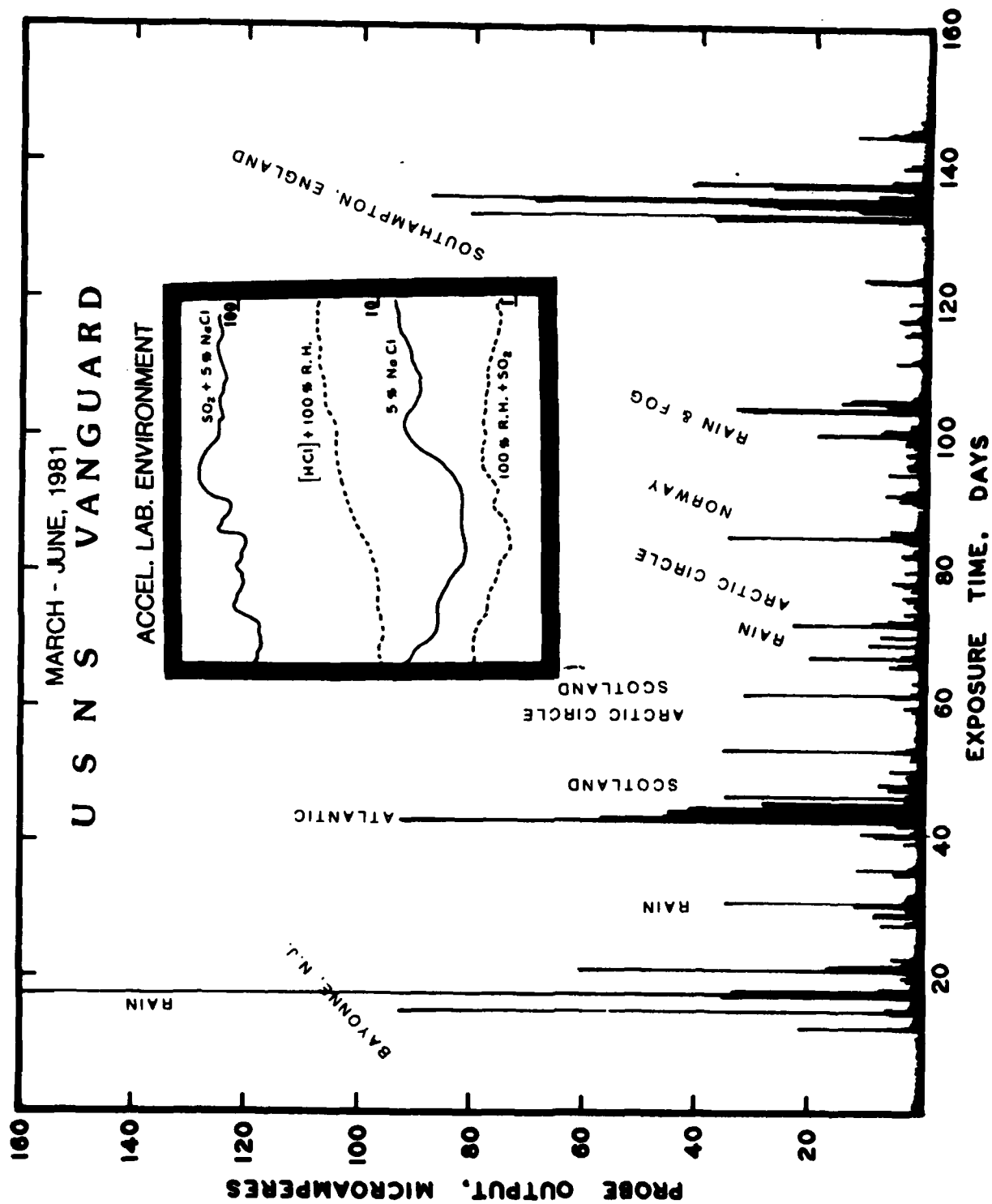


Figure 11. Plot of corrosivity monitoring aboard USNS Vanguard and in simulated laboratory environments.

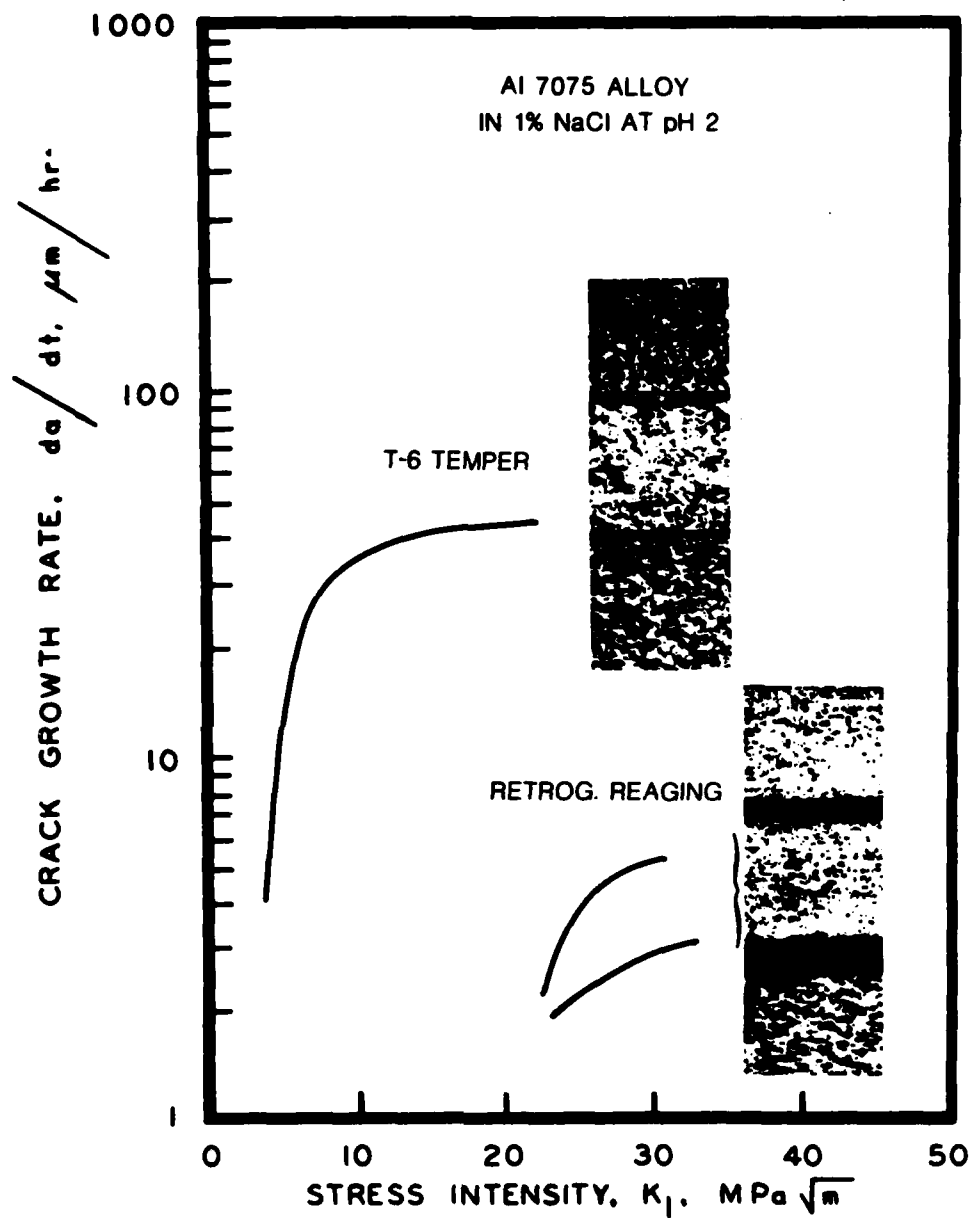


Figure 12. Effect of heat treatment on exfoliation and stress corrosion cracking behavior of 7075-T6 alloy.

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